

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#1/Declarator
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N. Butts

Applicants: Meluch et al.
Appl. No.: 09/767,558
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Title: MELT-SPUN POLYSULFONE SEMIPERMEABLE MEMBRANES AND
METHODS FOR MAKING THE SAME
Art Unit: 1723
Examiner: A. Fortuna
Docket No.: ACT-5612 CON of DIV I

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Commissioner for Patents
Washington, DC 20231

AFFIDAVIT OF SHMUEL STERNBERG UNDER 37 C.F.R. § 1.132

Sir:

I, Shmuel Sternberg, hereby state as follows:

1. I am currently an employee of Baxter International, Inc., holding the title of Baxter Distinguished Scientist. My educational background is as follows: B. CH.E - Georgia Institute of Technology (Georgia Tech); M.Sc. - Carnegie Institute of Technology (Carnegie-Mellon University); and Ph.D. - Case Western Reserve University. My professional experience is as follows: Amicon Corporation - Senior Engineer; Abcor Corporation (now Koch Membranes) - Manager, Materials Development; Millipore Corporation - Manager of Research; Memtek Corporation - Vice President of Research and Development; and Baxter Healthcare - Senior Technical Director, Baxter Distinguished Scientist. I have been involved in polymeric membrane research and development since my doctoral work in 1965 and throughout my industrial career.

2. I have reviewed U.S. Patent Application Serial No. 09/767,558 entitled "MELT-SPUN POLYSULFONE SEMIPERMEABLE MEMBRANES AND METHODS FOR MAKING THE SAME." I am familiar with polysulfone membranes and methods of making same.

3. I understand that the United States Patent and Trademark Office has rejected the claims of U.S. Serial No. 09/767,558 based on U.S. Patent No. 5,279,739 ('739 patent). I have reviewed the '739 patent.

4. The '739 patent relates to polymeric compositions useful in membrane technology. More specifically, the '739 patent relates to the fractionation of polymers to provide more chlorine resistant flexible polymers that can be used for the manufacture of membranes. The membranes that are envisioned by the '739 patent are designed for ultrafiltration.

5. The '739 patent is silent as to the exact formulations used to fabricate the example membranes. Rather, ranges of bath compositions and diluent solutions are provided, but one cannot make the specific membrane tested from the information in the patent. As one skilled in the art, I can state clearly, that the '739 patent does not disclose, or suggest, a melt-spinning process for making a membrane.

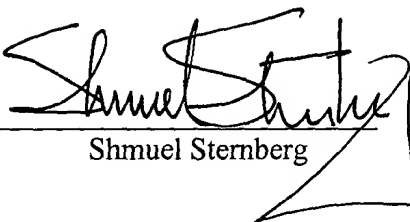
6. As one skilled in the art reviewing the '739 patent, I would not be led to a conclusion that a symmetric membrane would be created. Indeed, as one skilled in the art, I believe that the '739 patent is directed to the construction of an asymmetric membrane. In this regard, the patent discusses ultrafiltration and ultrafiltration membranes. All ultrafiltration membranes, to the best of my knowledge, include a layer of skin and are asymmetric. See, for example, *Handbook of Industrial Membrane Technology*, pp. 136-138 (attached hereto as Exhibit A) and *Membrane Handbook*, pp. 908 and 422 (attached hereto as Exhibit B).

7. Accordingly, to the extent that the '739 patent is being relied upon to disclose or even suggest to one skilled in the art, a membrane constructed from a melt-spun process or a symmetric membrane, the rejection is erroneous from a technical standpoint. The '739 patent does not disclose or suggest a melt-spun process. Nor would the '739 patent disclose or suggest to one skilled in the art the production of a symmetric membrane.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States

Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: Feb 27, 2002


Shmuel Sternberg

HANDBOOK OF INDUSTRIAL MEMBRANE TECHNOLOGY

Edited by

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Consultant
Pleasanton, California



NOYES PUBLICATIONS
Park Ridge, New Jersey, U.S.A.

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Ultrafiltration

Mark C. Porter

INTRODUCTION

The beginnings of ultrafiltration (UF) are coincident with that of reverse osmosis (RO) around 1960. Despite the fact that the term "ultrafiltration" first appeared in the colloid literature toward the end of the last century and Bechhold, in 1906 produced collodion membranes with pore sizes below 0.01 micron, these membranes were little more than laboratory curiosities. The hydraulic permeability was low and the pores were easily plugged.

The breakthrough, which resulted in an anisotropic RO membrane in 1959, paved the way for the first anisotropic UF membrane in 1963. Though UF membranes are porous and RO membranes are not, the evolutionary development of both occurred in parallel. Before 1960, membranes showing the retention properties of RO and of UF were available, but both had impractical filtration rates (flux).

In the years immediately following the end of World War II, the United States Government became concerned about shortages in water before the end of the century. The U.S. Department of the Interior set up the Office of Saline Water (OSW) and committed substantial financial resources to the development of various separation processes for water desalination. A significant portion of these funds was dedicated to the development of membranes for desalination—with funded programs continuing for over two decades (1950-1973). The result was one of the most promising large-scale processes for inexpensive desalination of seawater and brackish water—reverse osmosis (RO). It is no coincidence that the United States is a world leader, not only in RO, but also in those technologies that are direct spin-offs—namely UF and gas separations.

The first work in RO toward water-desalting was undertaken by Prof. Charles E. Reid¹ at the University of Florida in the mid-1950's. He discovered that cellulose acetate (CA) is semipermeable to seawater electrolytes.² The diffi-

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culty was that the water fluxes were too low to be interesting. Reid and co-workers attempted to cast thinner films, but found that below $6\ \mu$ in thickness, the films had defects which passed salt and were too fragile to handle.

Simultaneously, and unbeknownst to Reid, Sourirajan at the University of California, Los Angeles (UCLA) obtained the same results—94% salt rejection—but with water fluxes even lower than those reported by Reid.

Sourirajan's partner, Sidney Loeb, began to experiment with laboratory UF membranes (not fully asymmetric) made by Schleicher and Schuell of cellulose acetate (CA). Loeb heated the membranes under water (annealing) to temperatures between 80° to 90°C , thereby increasing the salt rejection from 0 to 92%, but the water flux decreased to unacceptable levels.

Loeb uncovered the work of a French investigator, Dobry³ in a literature search. Her work provided the clue which Loeb was looking for. Dobry dissolved acetylated CA in an aqueous solution of magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2$. This casting dope was spread as a thin film on a glass plate which was then plunged under water. The CA precipitated around the $\text{Mg}(\text{ClO}_4)_2$ leaving a porous film of CA. Eventually the $\text{Mg}(\text{ClO}_4)_2$ diffused out of the pores into the water bath. Loeb repeated Dobry's recipe, but the membranes were too porous and had no rejection for salt. He attempted to increase the ratio of CA to $\text{Mg}(\text{ClO}_4)_2$ but the casting solution viscosity was too high. The solution to the problem, suggested by Lloyd Graham, a UCLA graduate student, was to partially replace the aqueous $\text{Mg}(\text{ClO}_4)_2$ solution with acetone, a solvent for CA.

Loeb's standard casting solution contained CA, acetone, water, and $\text{Mg}(\text{ClO}_4)_2$ in the weight percentages of 22.2, 66.7, 10.0 and 1.1.⁴ When immersed in ice water, a high flux membrane was obtained albeit with low salt rejection (typically 5% or less). Loeb then annealed these membranes to 80°C to yield a salt rejection of 99%. The significant breakthrough was that the annealed membrane water-flux was 200 times greater than Sourirajan's CA films and 5 times greater than the annealed S & S membrane.

The reason for this breakthrough resided in the asymmetric structure of the membrane. When the product of the water flux and the total membrane thickness was calculated, the value was 666 times greater than Sourirajan's CA films. The most obvious explanation was that the *effective* membrane thickness was much less than the *total* membrane thickness. Loeb postulated the existence of a dense skin less than $1\ \mu$ in thickness supported by a relatively porous substrate. Thus, the substrate provided mechanical strength and the thin skin minimized the resistance to hydraulic permeability through the membrane. For the first time in history, it became possible to remove salt from water (95 to 98%) at pressures of 50 to 75 atmospheres with flux values of 10 to 15 gallons of product water per day per square foot of membrane area (GSFD).

In the early 1960's, the techniques utilized in the fabrication of asymmetric RO membranes were discovered to be applicable to the production of high-flux UF membranes with pores in the range of 10 to $1000\ \text{\AA}$ (see Figure P.1 in the Preface). Suddenly, UF on an industrial scale became practical. Macromolecular separation could be carried out at modest pressures (less than 6 atm.) with astonishingly high filtration rates.

Prof. Alan S. Michaels, of the Massachusetts Institute of Technology and the founder of Amicon Corporation, cast UF membranes from polyelectrolyte complex hydrogels in 1963. A joint development program between Amicon and

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Dorr-Oliver began to search for other polymers suitable for casting asymmetric UF membranes. By 1965, the first laboratory-scale UF membranes and cells appeared on the market. The ten-year period between 1965 and 1975 was a period of intense development where chemically and thermally resistant membranes were made from polymers like polysulfone (PS) and even polyvinylidene difluoride (PVDF) in molecular weight cut-offs (MWCO) from 500 to 1,000,000. Hollow fibers were also developed during this decade and a whole host of module configurations. Tubes, plate and frame units, and spiral-wound modules became available.

MEMBRANE STRUCTURE AND FABRICATION

Figure 3.1 is a cross section of a typical asymmetric (anisotropic) UF membrane. The prominent feature of these membranes is the thin skin on the surface—usually 0.1 to 1 μ in thickness. This thin skin permits high hydraulic permeability while the more open/porous substructure (typically 125 μ in thickness) provides good mechanical support. In addition, the pore configuration virtually eliminates internal pore-fouling. Since the minimum pore size is at the membrane surface, once a solute molecule gains entrance into the pore, it easily passes through to the other side of the membrane. The solute molecule sees an ever-widening pore channel with no restrictions or bottlenecks leading to entrapment.



Figure 3.1: Cross-section photomicrograph of asymmetric UF membrane.

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Membrane Handbook

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Membranes

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Allied Signal

POLYMER MEMBRANES

Membrane Fabrication

Membrane Modification

Characteristics of Commercially

Available Membranes

INORGANIC MEMBRANES

MEMBRANE CHARACTERIZATION

Membrane Porosity and Morphology

Surface Properties

ACKNOWLEDGMENTS

NOTATION

REFERENCES

Most ultrafiltration (UF) membranes are polymeric in nature, although recently inorganic membranes have also become available. The formation of an asymmetric membrane structure, i.e., an upper skin that is permselective and a more porous substructure for mechanical support, is an important element in the success of UF membranes. While many polymers, in particular, have been examined for use as membrane materials (Lloyd and Meluch 1985), only a few are widely used. Table 28-1 lists various polymeric and inorganic materials for UF membrane manufacture. Various polymer membranes have been reviewed by Pusch and Walch (1982), Kesting (1971), and Cabasso (1980a). An excellent review of inorganic membranes has been given by Hsieh (1988). An exhaustive list of membrane types made by various manufacturers has been compiled by Cheryan (1986). Table 28-2 lists product information from various UF membrane manufacturers. A list of manufacturers of UF membranes is given in Table 28-3.

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TABLE 28-1. Typical Ultrafiltration Membrane Materials.

Polymeric
Polysulfone
Polyethersulfone
Cellulose acetate
Regenerated cellulose
Polyamides
Polyvinylidene fluoride
Polyacrylonitrile
Inorganic
γ -Alumina/ α -Alumina
Borosilicate glass
Pyrolyzed carbon
Zirconia/Stainless steel or Zirconia/Carbon

POLYMER MEMBRANES

Membrane Fabrication

The most common UF membranes are based on polysulfone, cellulose acetate, polyamides, and various fluoropolymers. These are typically made by the phase inversion method in which

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the homogeneous polymer solution is converted to a porous polymer framework through exchange of the solvent with the precipitating nonsolvent. The asymmetric structure, which is responsible for the high fluxes, is composed of the thin, dense skin and a porous substructure. Wijmans et al. (1985) account for the formation of these two layers by two different phase separation phenomena:

1. Gelation for formation of the skin layer
2. Liquid-liquid demixing followed by gelation for the porous layer.

Gelation is induced by the concentration changes occurring on exchange of solvent for the precipitating liquid. The gelation of the bulk solution will be affected by the skin layer formation, which acts as a diffusion barrier (Strathmann and Kock 1977). The ternary phase diagram (polymer-solvent-nonsolvent) is a useful tool for understanding polymer membrane structure as a function of casting solution composition (Lonsdale and Kock 1977). Such phase diagrams have been obtained for casting systems of cellulose acetate, polysulfone (Wijmans et al. 1985), and polyphenylene oxide (Wijmans, Rutten, and Smolders 1985).

Membrane Modification

Hydrophobic polymers such as polysulfone or polyvinylidene fluoride may need to be modified to obtain higher fluxes, less fouling, etc. Some techniques are discussed by Cabasso (1980b). Methods of altering the surface chemistries are as follows:

1. *Reacting base polymer with hydrophilic pendant groups and then casting the membrane:* A common example is sulfonation of polysulfone with chlorosulfonic acid (Quentin 1973).
2. *Surface grafting of hydrophilic species on a previously made membrane:* This is difficult to do without damaging the base membrane by most chemical methods. Cabasso (1980b) describes sulfonation of a polysulfone hollow-fiber membrane using sulfuric

acid. Polyvinylidene fluoride (PVDF) can be reacted with compounds such as cellulose ether or inositol in alkaline medium (Madsen 1989). Polysulfone treatment with an NH_3 plasma and further reactions with chlorinated dyes in alkaline medium have been described (Wolff, Steinhäuser, and Ellinghorst 1988). Polyvinylchloride UF membranes have been made more hydrophilic by rf discharge treatment (Vigo, Nicchia, and Uliana 1988).

A simpler technique is to coat the base polymer membrane; for example, PVDF membranes can be coated with vinyl alcohol-vinyl acetate copolymer (Kasai and Koyama 1980). There are also reports of polyvinylpyrrolidone being entrapped in a polyetherimide matrix during casting; this increases the membrane hydrophilicity (Smolders 1989).

3. *Polymer blends:* Examples are blends of cellulose acetate with polystyrene and polyphenylene oxide phosphonate esters (Cabasso 1980b) and also a blend of poly(vinylidene fluoride)/cationic polyelectrolyte (Mir 1983). Membranes made by mixing inorganics and polymers have also been demonstrated and show improved pressure resistance (Kulprathipanja et al. 1988).

Characteristics of Commercially Available Membranes

Typical data with commercially available polysulfone and cellulose acetate (CA) membranes (Nadir/Hoechst) are shown in Table 28-4. The same polymer can be made in a wide range of surface porosities as illustrated for polysulfone in Figure 28-1. All these membranes were made with the same concentration of polysulfone in the casting solution; the solvents and casting conditions have been varied. Macrovoids can be induced in the porous substructure as shown in Figure 28-2 for the case of a polysulfone hollow-fiber membrane. Macrovoids generally lead to less mass transport resistance but limit operational pressure and may lead to defects under compression.

Table 28-4 shows that CA membranes typi-